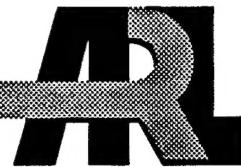


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High Rate Rechargeable Lithium Cells Employing Lithium Ion Conducting Solid Electrolytes

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ARL-TR-421

February 1995



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1. AGENCY USE ONLY (Leave blank)			2. REPORT DATE February 1995		3. REPORT TYPE AND DATES COVERED Technical Report: Jan to Dec 94	
4. TITLE AND SUBTITLE HIGH RATE RECHARGEABLE LITHIUM CELLS EMPLOYING LITHIUM ION CONDUCTING SOLID ELECTROLYTES			5. FUNDING NUMBERS PR: 62705 PE: H94			
6. AUTHOR(S) Edward J. Plichta and Wishvender K. Behl						
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Research Laboratory (ARL) Electronics and Power Sources Directorate (EPSD) ATTN: AMSRL-EP-PB Fort Monmouth, NJ 07703-5601			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-421			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER			
11. SUPPLEMENTARY NOTES						
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE			
13. ABSTRACT (Maximum 200 words) <p>Results are presented on high temperature solid state cells employing 50:50 weight percent lithium germanium vanadium oxide-lithium iodide. The incorporation of lithium iodide in lithium germanium vanadium oxide resulted in higher pellet conductivities and improved the high rate performance of the solid state cells. The cells were comprised of a lithium-aluminum or lithium-silicon alloy as the anode and a CVD thin film of titanium disulfide as the cathode. The cells exhibited an open circuit potential of about 2.1 V at 300 deg C and could be discharged at current densities up to 0.5 ampere per square centimeter.</p>						
14. SUBJECT TERMS Lithium germanium; vanadium oxide; lithium-aluminum; lithium-silicon; rechargeable lithium cell					15. NUMBER OF PAGES 16	
					16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified		20. LIMITATION OF ABSTRACT UL

CONTENTS

	page
INTRODUCTION.....	1
EXPERIMENTAL PROCEDURE.....	1
RESULTS AND DISCUSSION.....	3
CONCLUSIONS.....	6
REFERENCES.....	9

FIGURES

1. Schematic diagram of the cell stack.....	2
2. Arrhenius plots of conductivity for unsintered pressed pellets of $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ (a), 50:50 wt% $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI}$ (b), LiI (c) and sintered pellets of $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ (d).....	4
3. Discharge curve for the cell $\text{Li-Si}/\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4 - \text{LiI/TiS}_2$ at a current density of 30 mA/cm^2 at 300°C	5
4. Discharge curves for the cell $\text{Li-Si}/\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI/TiS}_2$ at current densities of 0.1 to 0.5 A/cm^2 at 300°C	8

TABLES

1. Discharge Characteristics of Li-Alloy/Solid Electrolyte/ TiS_2 Solid State Cells at a Current Density of 30 mA/cm^2 at 300°C	7
2. Cathode Capacities and Average Cell Voltages of the Cell $\text{Li-Si}/\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI/TiS}_2$ at Current Densities of 0.1 to 0.5 A/cm^2 at 300°C	7

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INTRODUCTION

Recently, we have described [1] a high temperature rechargeable lithium cell using a solid solution [2] of lithium germanium oxide (Li_4GeO_4) and lithium vanadium oxide (Li_3VO_4) as the lithium ion conducting solid electrolyte. The solid solution represented by the general formula, $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$, has been reported [3] to have a conductivity of about 0.08 S/cm at 300°C and was found [1] to possess an electrochemical stability range of over 4 V. The solid state cell was comprised of a lithium-aluminum alloy anode and a chemically vapor deposited (CVD) thin film of titanium disulfide as the cathode, and exhibited good discharge rate capabilities up to 100 mA/cm² and cycle life of over 200 cycles. Further improvements in the rate capabilities of the solid state cells are needed however in order to develop these cells as viable power sources for high rate pulse power applications. We have found that the rate capabilities of these cells can be substantially improved by using pressed pellets made with 50:50 wt.% mixtures of lithium iodide and $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ as the solid electrolyte. We have also investigated these cells using lithium-silicon alloys as the anode. The results of these studies are presented in this report.

EXPERIMENTAL PROCEDURE

The solid electrolyte, $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$, was prepared according to the procedure described [1] previously. Lithium iodide (Johnson Mathey - Alfa Chemicals) and lithium-aluminum (20 wt.% lithium) and lithium-silicon (48 wt.% lithium) alloys (Foote Mineral Company) were used as received.

The solid state cells were fabricated using unsintered pressed powder anode and solid electrolyte pellets. The anode pellet was prepared by pressing about 0.03 g sample of lithium-aluminum or lithium-silicon alloy powder in a 1.3 cm steel die at a pressure of 1800 kgs. A 0.05 g sample of the synthesized solid electrolyte powder, $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$, or a 50:50 weight percent mixture of $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ and LiI was then evenly spread on top of the pressed anode pellet in the steel die and further pressed at a pressure of 4,500 kgs. The thicknesses of both the anode and the electrolyte layers in the resulting pellet were about 200 microns each.

Thin films of titanium disulfide (TiS_2) on an aluminum substrate were used as the cathode. The films were prepared by chemical vapor deposition as previously described [4] and were approximately 25 microns thick with a calculated porosity of about 20% and coulombic capacity of 5.8 C/cm². The surface area of the cathode disks was 0.3 cm² resulting in a theoretical cathode capacity of 0.48 mAh based on 1 F/mole of TiS_2 .

The cells were assembled by stacking the titanium disulfide film on top of the anode-electrolyte pellet and placing the cell stack between two molybdenum disks which served as the current collectors. A description of the cell stack is shown in Fig. 1. The cell stack was held in compression through the use of a spring-loaded assembly and operated in a sealed Pyrex vessel under a flowing argon atmosphere as

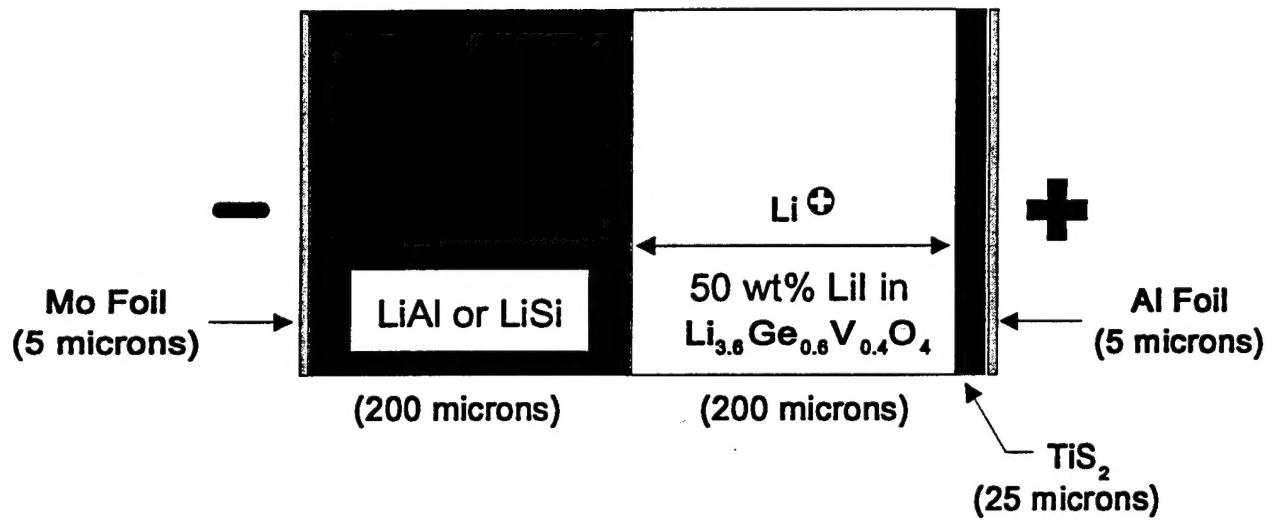


Figure 1. Schematic diagram of the cell stack.

described previously [5]. The other experimental details were similar to those described earlier [1].

The bulk conductivities of $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ and $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI}$ pellets were measured using a Wayne-Kerr model 6425 Precision Component Analyzer at a frequency of 1 kHz.

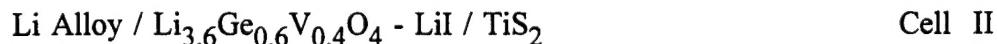
RESULTS AND DISCUSSION

The solid solutions of lithium germanium oxide (Li_4GeO_4) and lithium vanadium oxide (Li_3VO_4) are known [2] to be excellent lithium ion conductors. The conductivity of the solid solution represented by the general formula, $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$, has been reported [3] to be about 0.08 S/cm at 300°C. We have previously investigated solid state cells of the type:



employing unsintered pressed pellets of the solid solution, $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$, as the lithium ion conducting solid electrolyte. The conductivities of the unsintered pressed pellets of the solid electrolyte, $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$, were measured in the present studies and are plotted in Fig. 2 as a function of temperature up to 300°C. The conductivities of the solid electrolyte using sintered pellets were measured by Kuwano and West [2] and are included in Fig. 2. The conductivities of the pressed pellets obtained in the present studies were found to be significantly lower than the conductivities obtained with sintered pellets. However, due to the experimental difficulties involved in preparing thin (~ 200 um) sintered electrolyte pellets for high rate cells, we have attempted to improve the conductivities of the pressed pellets by the use of additives such as lithium iodide. The conductivities of pressed pellets of $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI}$ (50:50 wt.%) mixtures are plotted in Fig. 2 along with the conductivities of lithium iodide reported in the literature[6, 7]. It is seen that the conductivities of $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI}$ pellets are substantially higher than the conductivities of the pure $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ or LiI pellets and approach the conductivities obtained with sintered $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ pellets. The $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI}$ pressed pellets were found to be dense and compact which contributed to the enhancement in conductivity of the resulting pellets.

In order to improve the performance of cell I at high discharge rates, we have used the highly conducting $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI}$ pellets as the lithium ion conducting electrolyte in cells of the type:



using either lithium-aluminum or lithium-silicon alloy as the anode. The solid state cell exhibited an open circuit potential of about 2.1 V at 300°C. A typical discharge curve at a discharge current density of 30 mA/cm² is presented in Fig. 3. The cell

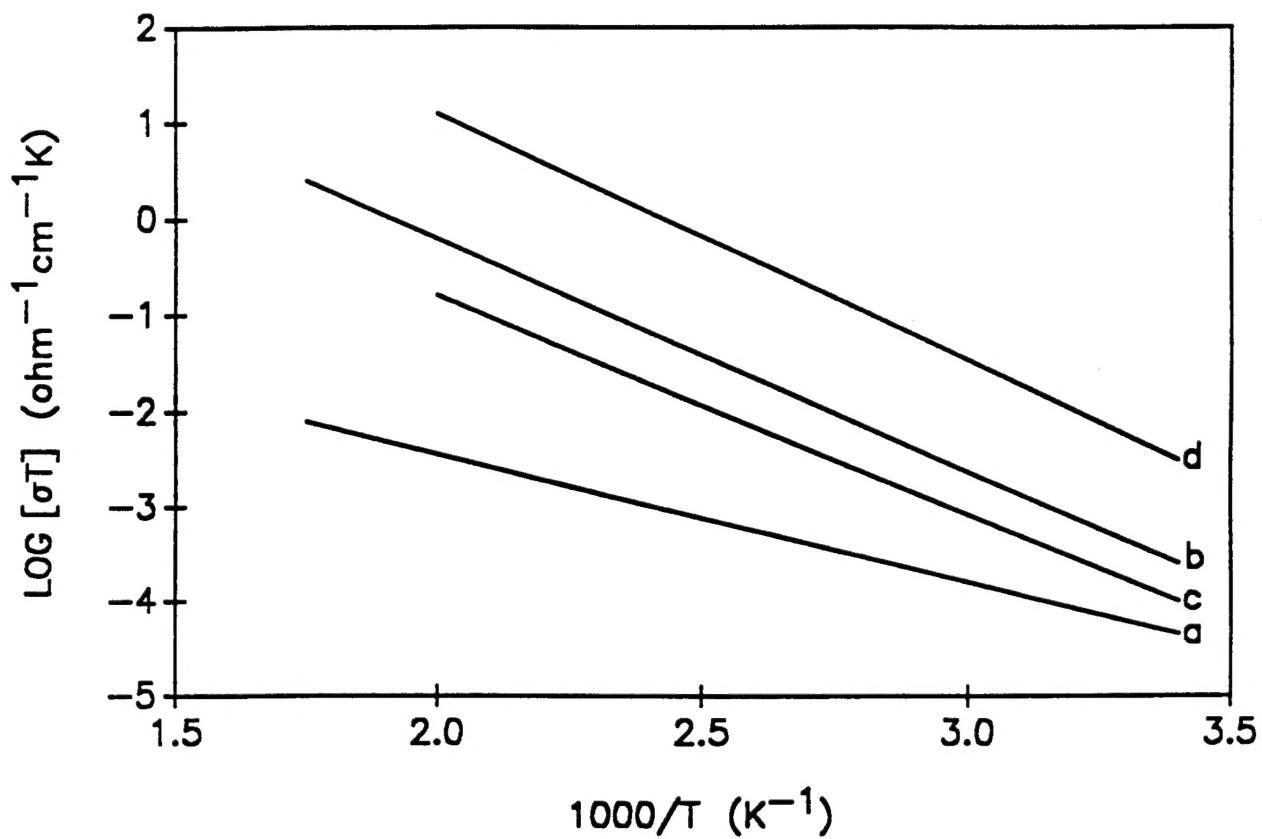


Figure 2. Arrhenius Plots of conductivity for unsintered pressed pellets of $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ (a), 50:50 wt% $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI}$ (b), LiI (c) and sintered pellets of $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ (d).

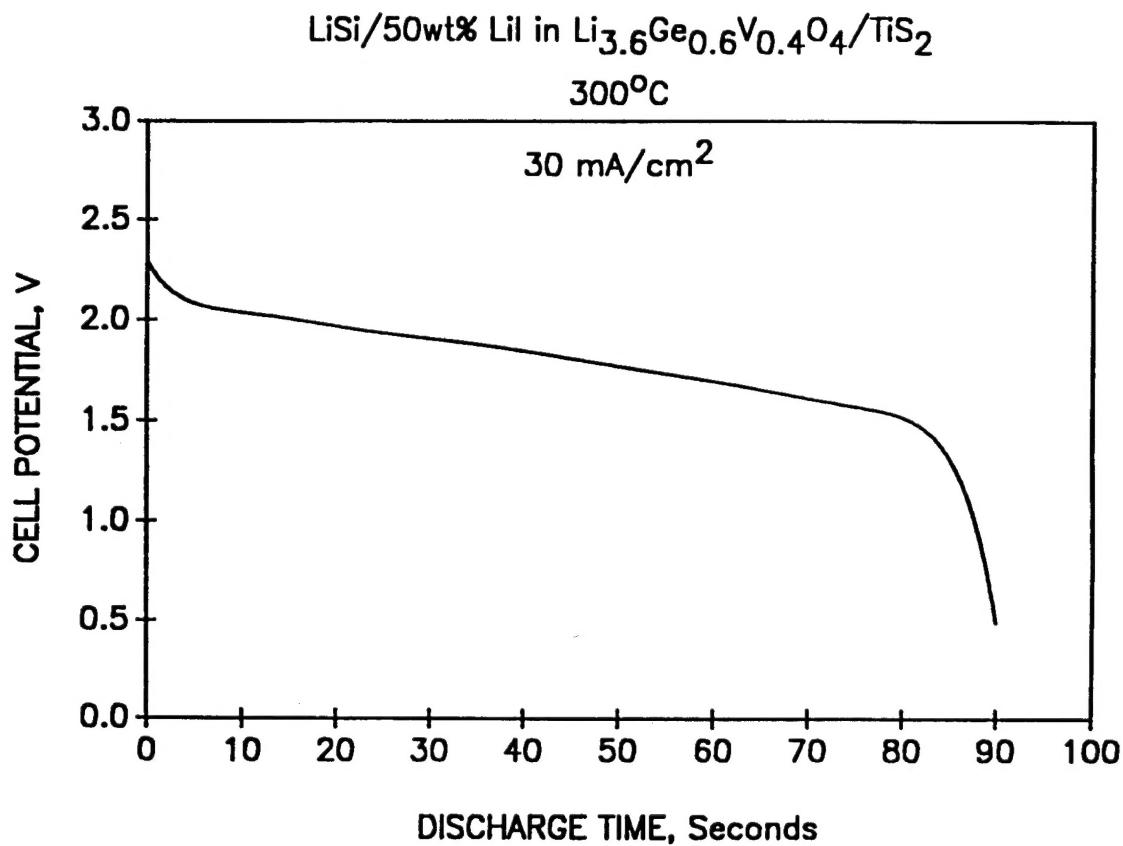
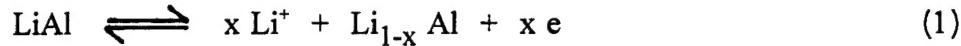


Figure 3. Discharge curve for the cell $\text{Li-Si/ Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI/TiS}_2$ at a current density of 30 mA/cm^2 at 300°C .

showed sloping discharge curves typical of the curves obtained with intercalating cathodes. The electrode reactions at the negative and positive electrodes on discharge may be represented as, respectively:



where $0 < x < 1$ and lithium ions are transported from left to right through the solid electrolyte and are intercalated into titanium disulfide according to the reaction given by Eq. 2. The reactions represented by equations 1 and 2 are reversed on charge and lithium is deintercalated from the titanium disulfide electrode and inserted into the lithium-aluminum or lithium-silicon alloy electrode. The cells were charged at a current density of 0.5 mA/cm^2 to a voltage of 2.3 V only in order to avoid any oxidation of the lithium iodide electrolyte which would occur at potentials above $\sim 2.4 \text{ V}$.

The average cell voltages, cell discharge times and cathode capacities obtained in Cells I and II at a current density of 30 mA/cm^2 using either lithium-aluminum or lithium-silicon alloy as the anode are summarized in Table 1. It is seen that the use of the highly conducting $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI}$ pellets as the electrolyte in Cell II results in a threefold improvement in cathode utilizations and cell discharge times over those cells employing pure $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ pellets as the electrolyte. The cell performance was found to be comparable at discharge rates up to about 0.1 A/cm^2 using either lithium-aluminum or lithium-silicon anode but the cells using lithium-silicon anodes exhibited lower polarization at higher discharge rates. Typical discharge curves obtained with the cell $\text{Li-Si/Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI/TiS}_2$ at current densities of 0.1 to 0.5 A/cm^2 are presented in Fig. 4. and the average cell voltages and cell capacities at various discharge rates are summarized in Table 2. The cells delivered cathode capacities of about 0.4 F/mole of TiS_2 at current densities of 0.1 and 0.2 A/cm^2 but showed increased polarization at higher current densities and delivered cathode capacities of only about 0.2 F/mole of TiS_2 .

CONCLUSIONS

The incorporation of 50 weight percent lithium iodide in $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ resulted in a 100-fold increase in conductivities of unsintered pressed pellets. The solid state cells employing highly conducting $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI}$ mixtures as the electrolyte, lithium-aluminum or lithium-silicon alloy as anodes and titanium disulfide as the cathode exhibited an open circuit potential of about 2.1 V at 300°C and showed excellent high rate capabilities with discharge rates approaching current densities of 0.5 mA/cm^2 .

Table 1. Discharge Characteristics of Li-Alloy/Solid Electrolyte/TiS₂ Solid State Cells at a Current Density of 30 mA/cm² at 300°C.

ANODE	ELECTROLYTE	DISCHARGE TIME (Sec)	AVERAGE VOLTAGE, V	CATHODE CAPACITY (F/mole TiS ₂)
LiAl	Li _{3.6} Ge _{0.6} V _{0.4} O ₄	27	1.02	0.14
LiSi	Li _{3.6} Ge _{0.6} V _{0.4} O ₄	25	0.88	0.13
LiAl	50wt% LiI in Li _{3.6} Ge _{0.6} V _{0.4} O ₄	81	1.38	0.42
LiSi	50wt% LiI in Li _{3.6} Ge _{0.6} V _{0.4} O ₄	90	1.72	0.47

Table 2. Cathode Capacities and Average Cell Voltages of the Cell Li-Si/
Li_{3.6}Ge_{0.6}V_{0.4}O₄-LiI/TiS₂ at Current Densities of 0.1 to 0.5 A/cm² at 300°C.

CURRENT DENSITY (A/cm ²)	CATHODE CAPACITY (F/mole TiS ₂)	AVERAGE VOLTAGE, V
0.1	0.41	1.35
0.2	0.40	1.03
0.3	0.23	0.97
0.5	0.19	0.86

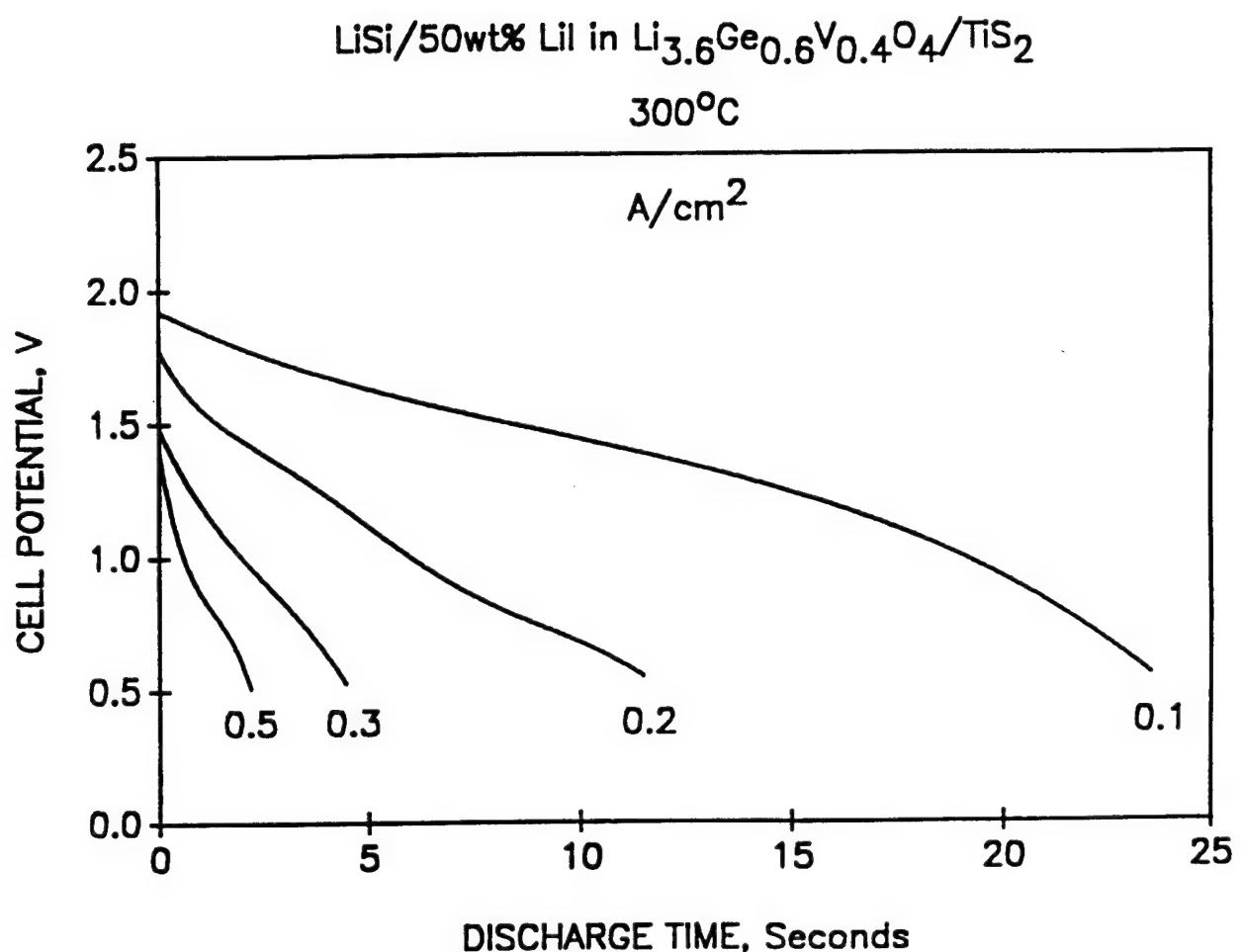


Figure 4. Discharge curves for the cell $\text{Li-Si}/\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4\text{-LiI/TiS}_2$ at current densities of 0.1 to 0.5 mA/cm^2 at 300°C .

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